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Investigation of magnetic, dielectric and electrical properties of Ba-hexaferrites

S Pervin¹, M M Rahman¹²*, F Ahmed¹ and M A Hakim³

¹Department of Physics, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh
²School of Engineering and Energy, Murdoch University, Murdoch, WA 6150, Australia
³Materials Science Division, Atomic Energy Centre, Ramna, Dhaka 1000, Bangladesh

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Abstract: Ba-hexaferrites of composition (BaO)₁₋ₓ (La₂O₃)ₓ 5.7 Fe₂O₃, where x = 0.00, 0.04, 0.08 and BaO 5.7 Fe₂O₃ + [0.7 wt% CaO + 0.3 wt% SiO₂] were prepared by standard double sintering ceramic technology using magnetite from Cox’s Bazar beach sand, Bangladesh. In this work, magnetic, dielectric and electrical properties of Ba-hexaferrites with and without additives have been reported. Measurements of permeability, loss factor, quality factor (Q-factor), resistivity and dielectric constant of the synthesized samples have been carried out. Permeability remains unaltered in the observed frequency range. The loss factor increases with the increase in temperature and additives as well. It has been observed that the loss factor decreases with the increase in frequency. The Q-factor decreases with the increase in temperature and increases with the increase in frequency. The dielectric constant decreases with the increase in frequency. The ac resistivity of Ba-hexaferrites increases with the increase in additive contents.

Keywords: Ceramic technology; Sintering; Magnetic properties; Dielectric properties; Resistivity

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1. Introduction

Ferrites are ceramic materials which fall in the category of ferrimagnetics and have great demands around the world owing to their wide range of practical applications [1]. Over the past few decades permanent magnets have been widely used with the introduction of hexagonal ferrites with composition MeFe₁₂O₁₉ where Me = Ba, Sr or Pb. These materials have a wide range of permanent magnetic applications such as the media for magnetic, magneto-optical recording, high frequency core materials and in some other technological applications [2, 3]. Hexaferrites are broadly used in permanent magnetic applications because of their cost effectiveness and better performances, high chemical stability, microwave devices, telecommunication, and high saturation magnetization [4–10]. Since the structural, electro-magnetic and dielectric properties of hexaferrites vary strongly with the composition, in this work, we have prepared Ba-hexaferrites (BaM) with following non-stoichiometric compositions: (BaO)₁₋ₓ (La₂O₃)ₓ 5.7 Fe₂O₃, where x = 0.00, 0.04, 0.08 and (BaO) 5.7 Fe₂O₃ + [0.7 wt% CaO + 0.3 wt% SiO₂]. There are enormous scopes of carrying out research with hexagonal permanent magnetic materials such as Ba-ferrites, Sr-ferrites or Pb-ferrites to upgrade their properties by changing the compositions. Up until now, numerous researches have been performed on hexagonal ferrites with and without additives [11]. Various synthesis techniques have been employed with various dopants to produce hexaferrites with enhanced properties suitable for applications [4, 5]. Babu et al. [12] studied the structural and hard magnetic properties of Ba-hexaferrites with the addition of La₂O₃ and reported that the magnetic properties of such ferrites have been improved remarkably with the addition of La₂O₃, which acts as grain refiner. Grossinger et al. [13] have studied the La–Co substituted Ba-hexaferrite and reported that the anisotropy as well as the coercivity increases with the increase in La–Co content. A large number of publications have been reported on these compositions.
materials owing to their widespread technological applications as smart tools for permanent magnets with various cationic substitutions [14, 15]. Many researchers around the world have performed significant contributions to enhance the electrical and magnetic properties of M-type hexaferrites by cationic substitutions for their useful technological applications [16, 17]. Simultaneous addition of Gd–Co on Ba-hexaferrites by Litsardkis et al. [18] indicates the presence of secondary phases, reduction of magnetization and an increase in coercivity with respect to the undoped Ba-hexaferrites (BaFe$_{12}$O$_{19}$). W. Yeping [19] has shown that Co–Ni, Co–Zn substitutions and V$_2$O$_5$ doping significantly causes to enhance the absorbing performance by modifying the static and dynamic properties of Ba-hexaferrites. However, till date the systematic study on the electrical and dielectric properties of rare-earth substituted M-type Ba-hexaferrites are very limited in literature [20, 21]. In the present study, magnetite from Cox’s bazar beach sand has been used as a major ingredient (about 85 %) for the manufacture of M-type Ba-hexaferrites with a small addition of rare-earth oxide (La$_2$O$_3$) and controlled amount of SiO$_2$ and CaO. Hence, in the present study we have emphasized on the possibility of developing M-type Ba-hexaferrites from the locally available raw materials. We have also reported the electrical and dielectric properties of synthesized hexaferrites. It is to be noted that many related works have been published recently [22–26].

2. Experimental details

Ba-hexaferrite powders were prepared from BaCO$_3$, La$_2$O$_3$, and Fe$_2$O$_3$ of Cox’s bazar beach sand, Bangladesh compositions of (BaO)$_{1-x}$ (La$_2$O$_3$)$_x$ 5.7 Fe$_2$O$_3$ where x = 0.00, 0.04, 0.08. 100 g batches of Ba-hexaferrite powders were also prepared with the addition of 1 g of (CaO + SiO$_2$). The chemicals were mixed thoroughly in motor and a pestle. To get a homogeneous mixture of the constituent chemicals and to reduce the particles size, powders were milled for 9.5 h using steel ball (in the ratio 1:6 powder to ball) in distilled water. The prepared slurry was dried, pelletedized and transferred to a porcelain crucible. The pellet was sintered at temperature of 1,235 °C for 4 h. The sintered materials were crushed to produce chemically homogeneous powder. The powders were milled again using an agate motor and a pestle for 3–4 h. By hydrostatic compaction the powder sample was pressed into desired shapes. Using a hydraulic press made of nonmagnetic stainless steel two different types of samples: cylindrical and pellets were prepared. X-ray diffraction (XRD) studies of Ba-hexaferrites were performed by a Philips X’PERT PRO X-ray diffractometer using Cu-K$_\alpha$ radiation in the range of 2θ = 15–75° in the steps of 0.02°. The phase and purity levels of Ba-hexaferrites sintered at 1,235 °C in air for 4 h were determined from the XRD patterns. From the XRD patterns, all the peaks were identified to be single-phase M-type structure with hexagonal symmetry (JCPDS data of PDF No. 84-0757) [27] without having any other intermediate phases. This confirmed the homogeneity and purity levels of the prepared samples [28]. The fundamental peak with maximum intensity for Ba-hexaferrites varies between 2θ = 32.52 and 32.62° at reflection (107) and d-spacing ranging from 2.7454 to 2.7530 Å. X-ray density, bulk density, porosity and unit cell volumes of the hexaferrites were calculated from the XRD analysis of the samples and were reported in Ref. [29].

Pellet shape samples with dimensions 10 × 3 mm were prepared at room temperature for electrical and dielectric measurements. The dielectric constant (ε') of Ba-hexaferrites was measured using 3255B precision magnetic analyzer. It provides 2-terminal measurement of inductors and transformers over the frequency range 20 Hz–650 kHz. Dielectric constant ε' was calculated from the relation: ε' = \frac{Cd}{\varepsilon_0A}, where C is capacitance of the pellet in Farad, d is the thickness of the pellet in meter, A is the area of cross section of the sample in m² and ε$_0$ is the free space’s permeability.

The real part of the complex permeability, loss factor, Q-factor of the Ba-hexaferrites was calculated using the following formula: μ = μ' – iμ", where μ' is the real part and μ" is the imaginary part of the complex initial permeability respectively expressed by the following equations:

\[ \mu' = \frac{B_0}{H_0} \cos \delta, \quad \mu'' = \frac{B_0}{H_0} \sin \delta. \]  

The ratio of the imaginary to the real part of the complex permeability is termed as the loss tangent or loss factor.

\[ \frac{\mu''}{\mu'} = \frac{(B_0/H_0) \sin \delta}{(B_0/H_0) \cos \delta} = \tan \delta. \]  

The reciprocal quantity of the loss factor is called the Q-factor which is given as

\[ Q = \frac{1}{\tan \delta}. \]

3. Results and discussion

Figures 1 and 2 show the real part of the complex permeability of Ba-hexaferrites with compositions (BaO)$_{1-x}$ (La$_2$O$_3$)$_x$ 5.7 Fe$_2$O$_3$ for x = 0.00, 0.04, 0.08 and BaO 5.7 Fe$_2$O$_3$ + [0.7 wt% CaO + 0.3 wt% SiO$_2$] respectively sintered at 1,235 °C in air for 4 h in the frequency range 1–600 kHz. According to the permeability data presented in...
Figs. 1 and 2, it has been found that the initial permeability of Ba-hexaferrites increases with the addition of La$_2$O$_3$ and (CaO + SiO$_2$). It may be stated that with a small addition of La$_2$O$_3$ to the Ba-hexaferrites the density might have been increased, leading to an increase in the permeability. Our result is in agreement with the previous standard results for ferrites with higher density and larger average grain size possess a higher initial permeability [30]. Throughout the investigation, we observed that the real part of the complex initial permeability remains almost unaffected over the entire frequency range. Introduction of La$_2$O$_3$ and (CaO + SiO$_2$) causes to an increase in permeability, which might be related to the fact that it causes to a decrease in hyperfine fields at 12 k and 2b sites which in turn results to a decrease in the strength of superexchange interaction Fe$^{3+}$–Fe$^{2+}$ [31, 32]. This might also cause magnetic dilution by enhancing the production of Fe$^{2+}$ ions.

Figures 3 and 4 show the temperature dependence of loss factor of Ba-hexaferrites with and without additives. According to the diagrams, it has been observed that the loss factor of Ba-hexaferrite samples decreases with the increases in La$_2$O$_3$ addition. The same nature of the loss factor has been noticed while a controlled amount of CaO and SiO$_2$ have been added simultaneously to the pure Ba-hexaferrites. Moreover, the loss of Ba-hexaferrites has been found to be decreased with cooling.

Figures 5 and 6 show the variation of loss factor of the Ba-hexaferrites with and without additives as a function of frequency. This measurement has been done over the frequency range 1–500 kHz. At very low frequency like (1 kHz), the loss factor is high and it starts decreasing with the increase in frequency and at high frequency region it becomes almost unaffected with the further increase in frequency. In magnetism, the study of energy loss is very important, since the amount of energy wasted on processes other than magnetization can prevent the AC applications of a given material. Loss factor measures the inefficiency of a magnetic system and obviously should be as low as possible. At high frequencies, losses are to be lower if
domain wall motion is inhibited and the magnetization is forced to change by rotation [33]. Our observation has been found to be consistent with the Q-factor studies (Figs. 7, 8), where it is observed that the Q-factor increases with the substitutions. This reflects the fact that with the addition of rare-earth oxide and (CaO + SiO$_2$) the loss of energy has been reduced. The decreasing nature of the loss factor attributes the relaxation phenomena of magnetization of domain wall [34]. Addition of rare-earth (RE) elements for the substitution of Ba$^{2+}$ ions results in a smooth decrease of magnetization comparing to the pure hexaferrites [35, 36]. Moreover, introduction of RE oxides to the Ba-hexaferrites disrupts and weakens the Fe$^{3+}$–O–Fe$^{3+}$ superexchange interaction and thereby accelerating the Fe$^{2+}$ ions production and spin canting as well [31, 32]. It is believed that due to these combined effects the loss factor of Ba-hexaferrites is decreased. Some sort of distortion in the lattice structure might come into play to cause the internal stresses to the hexaferrites [37, 38]. Figures 7 and 8 show that the Q-factor of Ba-hexaferrites increases with the addition of La$_2$O$_3$ and simultaneous addition of CaO and SiO$_2$ with pure samples which is consistent with our loss factor measurements (Figs. 5, 6, 7, 8). Figures 9 and 10 show the variation of Q-factor as a function of frequency for the same samples. It is observed that Q-factor increases with increasing frequency. According to the study of loss factor and Q-factor, we observed that at low frequency region Ba-hexaferrites work as a better permanent magnetic material with low losses and high qualities. The variation in Q-factor with temperature and frequency may also be explained in the same way as that of the loss factor, which is already been mentioned previously. Loss tangent is high at lower frequency which is well-known as the inter-facial polarization [39]. The dielectric loss of SrBa-hexaferrite with the substitution of Ce–Ni content...
show the normal dielectric explained in terms of electron-hopping among the Fe\(^{2+}/Fe^{3+}\) ions at the octahedral site [40].

Figures 11 and 12 show the variation of dielectric constant with frequency from 1 to 650 kHz at room temperature. The dielectric constant decreases with increasing frequency and with addition of La\(_2\)O\(_3\) and (CaO + SiO\(_2\)), which is rapid at lower frequencies and slower at higher frequencies. This result is very similar to that reported earlier [41]. At higher frequency, around 300 kHz and above dielectric constant of Ba-hexaferrites become almost independent of frequency. This is a normal dielectric behavior observed in most of the ferromagnetic materials, which may be due to the interfacial polarization as...
predicted by Koops theory Maxwell and Wagner bilayer model [42]. The dielectric behaviour of ferrites, generally, may be elucidated on the basis of various mechanisms of dielectric polarization, which is similar to the conduction mechanism that arises from the electronic exchange between Fe$^{3+}$ and Fe$^{2+}$ [43, 44]. The same phenomenon has been reported by Rabinkin and Novikova [45]. The electronic conduction in ferrites occurs basically due to the hopping of electrons between the ions of the same element existing in more than one valence state which are distributed randomly over the crystallographically equivalent lattice sites. Polycrystalline ferrites are considered to have two layers—first one being a heterogeneous medium of conducting layer with a large number of grains and the other one is a highly resistive thin layer with grain boundaries [46, 47]. The interfacial dielectric polarization arises from defects in grain boundaries, oxygen vacancies, dislocations and other defects that cause to an enhancement of dielectric constant at lower frequencies [48]. Higher value of dielectric constants results in a decrease in skin depth of electromagnetic waves by increasing the skin effect. For this reason, ferrites with lower dielectric constant find their potential applications at high frequency devices [42, 49].

The ac resistivity of (BaO)$_{1-x}$-(La$_2$O$_3$)$_x$ 5.7 Fe$_2$O$_3$, where $x = 0.00$, 0.04, 0.08 and BaO 5.7 Fe$_2$O$_3$ + [0.7 wt% CaO + 0.3 wt% SiO$_2$] samples sintered at 1,235 °C for 4 h in air has been represented in Figs. 13 and 14 in the frequency range of 5–500 kHz. It has been observed that the ac resistivity of Ba-hexaferrites increases with the addition of La$_2$O$_3$ and (CaO + SiO$_2$). The increase in resistivity might happen due to the increase of porosity of Ba-hexaferrites with the addition of La$_2$O$_3$ and (CaO + SiO$_2$). Since pores are nonconductive, causing the increase in resistivity of the materials [50]. All the curves show the significant dispersion with frequency, which is an important behaviour of ferrimagnetic materials. The increase in frequency enhances the hopping frequency of charge carriers resulting in an increase in the conduction process thereby decrease the resistivity. The minimum resistivity occurred when the frequency of the hopping charge carriers is equal to the applied field frequency termed as resonance frequency i.e., the jumping frequency of hopping charge carriers are almost equal to that of the applied field. Then again with the increase in frequency, the resistivity increases most linearly which may be due to the retardation of hopping charge carriers with increasing applied field frequency. From this investigation we observe a rapid dielectric dispersion at lower frequency region and it becomes almost independent in the higher frequency values. The dielectric behaviour of ferrites has been already explained on the basis of the mechanism of the dielectric polarization that has been found to be similar to that of conduction process in the discussion of dielectric properties.

4. Conclusions

Addition of La$_2$O$_3$ and [0.7 wt% CaO + 0.3 wt% SiO$_2$] to Ba-hexaferrites has been found to play very significant role in improving magnetic, electrical and dielectric properties
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The samples increases with the additives which in turn causes to an increase in initial permeability of the samples. It has been also noticed that the real part of complex permeability remains almost invariant with the observed frequency range signifying that no domain wall motions occur at the high frequency region. The observed decrease in dielectric constant with increase in frequency is due to the fact that above certain frequencies the electronic exchange between Fe$^{2+}$ and Fe$^{3+}$ ions does not follow the frequency of the applied ac field. The dielectric constant decreases with increasing frequency, which is rapid at lower frequencies and slower at higher frequencies. This is a normal dielectric behaviour observed in most of the ferrimagetic materials. The ac resistivity decreases with increasing frequency and become independent in the higher frequency region. The loss factor increases with increasing temperature and decreases with increasing frequency. For inductors used in filter applications, the quality factor is often used as a measure of performance. The Q-factor decreases with increasing temperature and increases with increasing frequency. It is believed that La$_2$O$_3$ acts as a grain refiner and CaO promotes the plate like grain growth oriented perpendicular to the basal plane while SiO$_2$ activates the reaction kinetics. The La$_2$O$_3$ substituted hexaferrites have the enhanced magnetic, dielectric and electrical properties due to the fact that substituent ions for Fe$^{3+}$ accounts the ionic radii of the elements thereby causing new types of interactions and thus improving the desired properties of the synthesized samples.

References

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